Thermal Science and Engineering Progress 64 (2025) 103840

Contents lists available at ScienceDirect

Thermal Science and Engineering Progress

journal homepage: www.sciencedirect.com/journal/thermal-science-and-engineering-progress

Experimental and numerical study of suppression synergistic mechanism of Novec1230 and Trans-1233zd

Biao Zhou [a,e,*], Xuyao Wang [a], Hideki Yoshioka [b], Kai Wang [a], Dezheng Wang [a], Xin Huang [c], Tao Chen [d], Yi Li [d,*]

[a] School of Emergency Management and Safety Engineering, China University of Mining and Technology (Beijing), Beijing 100083, China
[b] Department of Architecture, Faculty of Engineering, The University of Tokyo, Tokyo 113-8654, Japan
[c] Center for Aircraft Fire and Emergency, Civil Aviation University of China, Tianjin 300300, China
[d] Tianjin Fire Science and Technology Research Institute of MEM, Tianjin 300381, China
[e] Inner Mongolia Research Institute, China University of Mining and Technology (Beijing), Ordos 017010, China

A R T I C L E I N F O

Keywords:
Minimum fire-extinguishing concentration
Novec1230
Trans-1233zd
Synergistic effect
Chemical fire agents

A B S T R A C T

Novec 1230 is considered to be the most promising halon alternative recently because of the low Global Warming Potential (GWP) and minimum extinguishing concentration (MEC). However, the fire suppression performance is believed to be strengthened with the mixed chemical gas agents. With an aim to prob the flame suppression effect of mixed fluorinated chemical gas, this study combined Novec 1230 and *trans*-1233zd, carried out a series of experiments, studied MEC, and proposed the potential synergistic mechanism between the two gases. The MEC is tested by using a bench scale of cup burner platform. When the volume fraction of *trans*-1233zd is 80 %, 60 %, 50 %, 40 % and 20 %, the MEC of the mixed chemical gas is 7.0 %, 6.5 %, 6.2 %, 5.9 % and 5.7 %. In addition, the synergistic effect model was calculated theoretically and set up on the basis of experimental results. The synergistic factor F has a minimum value of 0.94 when the volume fraction of *trans*-1233zd is 20%. The synergistic effect is found to be obvious because the experimental value is much lower than the theoretical value. Then, the study analyzed the synergistic mechanism between Novec 1230 and *trans*-1233zd at the molecular level using the Gaussian 16 code. The results showed that the reaction between the pyrolysis products of Novec 1230 and *trans*-1233zd produced more $\cdot CF_3$, $\cdot C_2F_5$ and $\cdot C_3F_7$ groups, which helps to consume the free radicals in the fire scene and achieve the blocking of the chain reaction. This study provides valuable guidance for the application of Novec 1230 and new fluorine-containing gas mixture in fire extinguishing, which will be helpful for the research and development of new chemical gas fire extinguishing agents in the future.

1. Introduction

Chemical gas fire extinguishing agents are widely used in libraries, cultural heritage protection, aerospace, and electrical fields [1–3]. As the environmental situation becomes increasingly severe, traditional chemical gas fire extinguishing agents are gradually restricted. The fire suppression mechanism and performance of chemical gas have been investigated for several years by a great many researchers [4–14]. These studies mainly focus on testing the performance of pure fluorinated chemical gases, among which Novec 1230 is considered to be a new generation of chemical gas fire extinguishing agent that takes into account both fire extinguishing efficiency and environmental friendliness. Perfluoro-2-methyl-3-pentanone (Novec 1230), a fluorinated ketone with the structural formula $CF_3CF_2C(=O)CF(CF_3)_2$ [15], is a fire-extinguishing agent with numerous advantages and has been used in various fields [7]. The boiling point is 49 ℃ which may delay atomization efficiency and reduce the fire-extinguishing efficiency during the total flooding fire-fighting process. Trans-1-Chloro-3,3,3-Trifluoropropene (*trans*-1233zd(E)), with the structural formula $ClCH=CHCF_3$, is a kind of fluorinated chemical gas with a boiling point of 19 ℃, a Global Warming Potential (GWP) of 1, and an Ozone Depletion Potential (ODP) of 0 [16]. According to previous research [17], the C-Cl bond of *trans*-1233zd is easily broken and produces Cl radical, which can combine with ·H and ·OH in the fire to block the chain

* Corresponding authors.
E-mail addresses: zhoubiao1088@cumtb.edu.cn (B. Zhou), 15688166632@163.com (X. Wang), yoshioka@arch1.t.u-tokyo.ac.jp (H. Yoshioka), 346153141@qq.com (K. Wang), misaka.arron1315@gmail.com (D. Wang), x-huang@cauc.edu.cn (X. Huang), chentao@tfri.com.cn (T. Chen), liyi@tfri.com.cn (Y. Li).

https://doi.org/10.1016/j.tsep.2025.103840
Received 3 January 2025; Received in revised form 28 May 2025; Accepted 5 July 2025
Available online 6 July 2025

reaction. Currently, researchers have conducted studies on the fire inhibition ability of *trans*-1233zd [18–20]. These studies demonstrate that the substance has potential for application in the firefighting field.

Since Novec 1230 belongs to the Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS), which are unfriendly to the environment, and have a flame-promoting effect at low concentrations [8,21], this has hindered its application in some fields. Studies find composite fire extinguishing agents can improve the performance of single ones [22–27]. Therefore, some researchers have tried to combine chemical gases with other substances to overcome their drawbacks. The main emphasis of currently available researches focus on the synergy with inert gases [28–32], fine water mist [33], flame retardants [34] and other organic substances [35,36] and so on. Although many achievements have been made in the synergistic research on Novec 1230, there are few reports on the synergistic flame suppression with other new chemical gases available. Existing research is also limited to analyzing and discussing macroscopic phenomena, lacking the exploration of synergistic mechanisms at the molecular level. To further study the flame suppression effect of mixed fluorine chemical gases, this study introduced quantum chemical calculations to simulate the reactions between pyrolysis products of Novec 1230 and *trans*-1233d based on fire extinguishing experiments, which contributes a deep understanding of the synergistic mechanism.

In this paper, a detailed understanding of the flame suppression performance of Novec 1230/*trans*-1233zd mixed chemical gases was newly discussed by using a bench scale of a cup burner platform, and the influence of changed ratios on flame suppression was described. Furthermore, this study explores the synergistic mechanism of the mixed chemical gas at the molecular level. The reactions between the pyrolysis products were analyzed by using the Gaussian 16 code. The results of quantum chemical calculations need more experiments to be further verified. This study benefits the development of advanced, efficient, and environmentally friendly fire extinguishing agents.

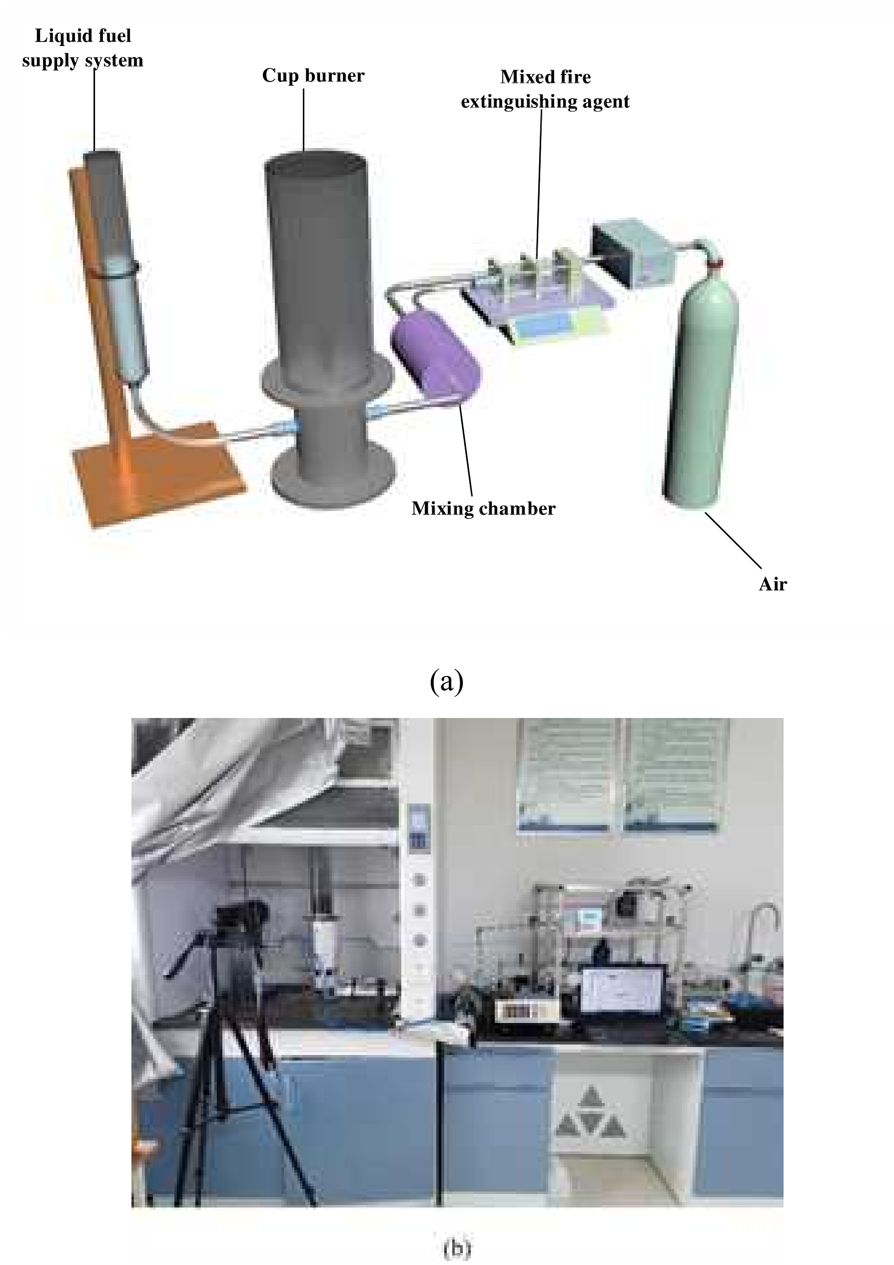


Fig. 1. Experimental setup diagram. (a) Experimental platform structure (b) Experimental platform in reality.

2. Test and methods

2.1. Test facility

The minimum fire extinguishing experimental platform was constructed based on the fire extinguishing principle of chemical gas, as shown in Fig. 1. The experimental platform includes a cup burner, mixing and heating system, fuel supply and a video camera. In this study, D07-7 mass flowmeters manufactured by Beijing Sevenstar Electronics Co.Ltd were used. The study also used an electronic balance which can record mass changes of 0.01 g per second and a syringe pump that pushes 0.01 mm per minute. This allows for precise control of extinguishing media input. The video camera was a Canon Co. LTD EOSR7. The video of the experiment was recorded at 1080P 100 fps to ensure that the flame image was clear and recognizable. The experimental apparatus are shown in Table 1**.**

2.2. Test materials

The basic information of the chemical gas used in this test was shown in Table 2. The purities of Novec 1230 and *trans*-1233zd were better than 99.9 % in mass fraction. All samples were used directly without any further purification. The alcohol used in the fire extinguishing experiment was produced by Jiaxing ZhongHao Chemical Co. LTD, with a concentration of 99.0 %.

The tests for the determination of the minimum fire-extinguishing concentration (MEC) were based on the ISO 14520 standard and related test methods. Before the experiment, Novec 1230 and *trans*-1233zd were configured as a mixture of extinguishing media in volume fractions as shown in Table 3. The ambient temperature during the experiment was 15 °C. Under this condition, Novec1230 and *trans*-1233zd were liquid and miscible. According to the volume ratio after vaporization in the mixing chamber, the required mass of each of the two agents was calculated and mixed to form a mixed agent. The liquid in the mixing chamber can be instantly vaporized to form a mixed gas to achieve the required ratio. Set the air flow rate to 10 L/min through the mass flowmeter, and heated the mixing chamber to keep its temperature at 90 ℃ to ensure the fire extinguishing media can be gasified quickly after entering [37]. By heating the pipeline and detecting the temperature at the cup burner outlet, it is ensured that the mixed agent can participate in the combustion in a gaseous state. Igniting the ethanol in the cup burner and using the syringe pump to pass the extinguishing media into the cup burner after the flame has stabilized. Waiting for 30 s, if the flame is not extinguished, adjust the speed of the syringe pump so that the amount of extinguishing media fed into it gradually increases. Repeat the above process until the flame is extinguished. High-precision balances were used to monitor changes in the mass of liquid extinguishing media. **Eq. (1)** was used to calculate the volume of extinguishing media gasification, thus obtaining the minimum extinguishing concentration of the gas mixture. In the present work, a series of tests varying volume ratios of Novec 1230 and *trans*-1233zd under 10 L/min of airflow were conducted.

The extinguishing concentration of the mixed fire extinguishing media was determined as follows.

Table 1
Experimental apparatus.

Instrument	Accuracy	Manufacturer
D07-7 mass flowmeters	0.1 L/min	Beijing Sevenstar Electronics Co. Ltd
QHZS-001A syringe pump	0.01 mm/min	Yuanhangdongli Co. LTD
YH-30 high-precision balance	0.01 g/s	Wuxianliang Co. LTD
EOS R7 Camera	1080P 100FPS	Canon Co.LTD

Table 2
Basic properties for the chemical gas.

Chemical Gas	Novec 1230	Trans-1233zd
GWP	1	1
ODP_{100yr}	0	0.00034
BP[℃]	49	19
Purity[wt%]	＞99.9 %	＞99.1 %
Manufacturer	Zhejiang Noah Fluorochemical Co.Ltd	Zhejiang Noah Fluorochemical Co.Ltd

Table 3
The initial ratios of Novec1230 and *trans*-1233zd mixed extinguishing media.

Test No.	Volume fraction of Novec1230	Volume fraction of *trans*-1233zd
1	0.00 %	100.00 %
2	20.00 %	80.00 %
3	40.00 %	60.00 %
4	50.00 %	50.00 %
5	60.00 %	40.00 %
6	80.00 %	20.00 %
7	100.00 %	0.00 %

$$C = \frac{V_{mixture}}{V_{mixture} + V_{Air}} \times 100\% \quad (1)$$

where $V_{mixture}$ and V_{Air} are the volumetric flow rates (L/min) of mixed fire extinguishing media and air, respectively.

2.3. Computational methods

Gaussian 16 is a quantum chemistry calculator that is used to study the structure and properties of molecules and chemical reaction processes [38]. Molecular geometries, energies, spectra, and other properties, as well as analysing reaction mechanisms and calculating transition states can be simulated. The software supports a wide range of computational methods and basis sets and is suitable for studies ranging from simple molecules to complex systems.

The study of the synergistic mechanism of fire extinguishing needs to go deeper at the molecular level. Obtaining information on the potential energy surface is important to study the reaction mechanism [39]. According to previous research, density functional theory (DFT) has been a common method for calculating the potential energy surface [40–42]. It has the advantages of small computational volume, high computational accuracy, and fast computational speed.

In this paper, the reaction pathways of the pyrolysis products of Novec 1230 and *trans*-1233zd were calculated using the Gaussian 16 code. The structure optimization, frequency analysis, and transition states were simulated by using the density-functional method of B3LYP and the basis group of 6–311++G (d, p). Parameters such as vibrational frequencies, bond angles, etc. were obtained from the calculations. The vibrational frequency analysis of the transition state has a unique imaginary frequency, which proves the correct transition state. Intrinsic reaction coordinate (IRC) was carried out later using the same calculation method and basis set to verify the correctness of the reaction path. Energy bases were obtained by single-point energy calculations. The effect of ethanol decomposition on the reaction was not considered in the calculation. Only the reaction between the pyrolysis products of Novec 1230 and *trans*-1233zd was discussed.

2.4. The description of synergistic calculation theory

Pure chemical gas extinguishing media have certain limitations. The synergistic action of multiple extinguishing media can improve the efficiency of fire suppression and reduce the generation of environmental hazards. Lott [43] proposed a hypothetical calculation of the synergy factor for mixed extinguishing media, as shown in **Eq. (2)**:

$$F = \frac{n_1}{n_1^0} + \frac{n_2}{n_2^0} \tag{2}$$

where, n_1^0 and n_2^0 are the molar amounts required to extinguish the flame with pure extinguishing media 1 and 2, respectively. n_1 and n_2 are the molar amounts of each of the two mixed extinguishing media after reaching the extinguishing concentration.

Synergy factor F is the key basis for determining whether extinguishing media 1 and 2 has a synergistic effect. If $F < 1$, there is a positive synergistic effect. If $F > 1$, there is a negative synergistic effect. If $F = 1$, there is no synergistic effect of extinguishing media 1 and 2 in the fire extinguishing process. When $F = 1$, it is assumed that there is no synergistic effect of the two fire extinguishing media. Therefore, the theoretical MEC equation, which assumes no synergistic effect of the two extinguishing media is proposed, just as shown in **Eq. (3)**:

$$\frac{C}{100 - C} = \frac{1}{\frac{X(100 - C_1^0)}{C_1^0} + \frac{(100 - C_2^0)(1 - X)}{C_2^0}} \tag{3}$$

where, C is the theoretical extinguishing concentration of mixed fire extinguishing media without considering synergistic effect, C_1^0,C_2^0 are the extinguishing concentrations of pure extinguishing media 1 and 2. X is the molar percentage of extinguishing media 1 in the mixed extinguishing media.

In summary, the assuming no synergistic effect theoretical MEC of Novec1230 and *trans*-1233zd mixed extinguishing media and synergistic effects can be determined by calculating. In this paper, Novec1230 is set as fire extinguishing media 1 and *trans*-1233zd as fire extinguishing media 2.

3. Results and discussion

3.1. Test results of pure chemical fire suppression performance

Fig. 2 gives the flame morphology of Novec 1230 and *trans*-1233zd during suppressed combustion. The flames became bright and increased in height at the initial stage of media introduction. Novec 1230 and *trans*-1233zd enhanced combustion at low concentrations [21]. When the time approached 30 s, the root of the flame began to shake and grew more violent as the time increased. The root of the flame jumped up and was extinguished when the time reached 90 s. In the calibration test, the MEC of Novec 1230 is measured to be 5.62 %, which agrees with the previous test [37]. The MEC of *trans*-1233zd was measured as 7.60 %.

3.2. The results of synergistic fire suppression performance

Fig. 3 reflects the variation of flame pattern for Novec 1230 and *trans*-1233zd mixed fire extinguishing media at different ratios. The overall trend of the flame height shows an increase and then a decrease,

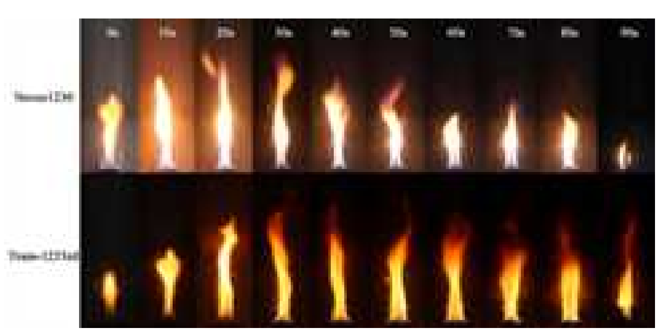


Fig. 2. Flame patterns of pure Novec1230 and tran-1233zd in action.

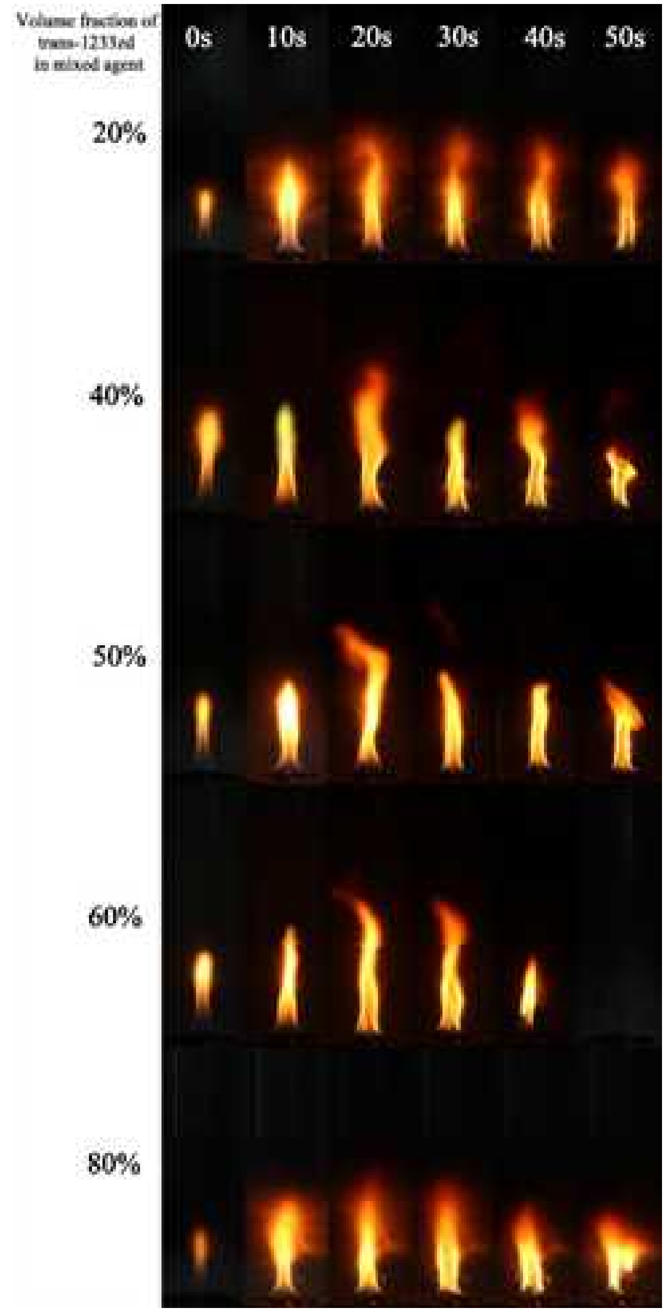


Fig. 3. Flame patterns varying with different volume fractions of *trans*-1233zd in mixed media.

which is consistent with the characteristics of Novec 1230 and *trans*-1233zd. It can be seen the enhanced combustion phenomenon is more significant when *trans*-1233zd is 40–60 % of the mixture than at 20 % and 80 %, and there is a significant increase in the flame height. The flame height was measured, and the results are shown in Fig. 4. When the percentage of *trans*-1233zd is 20 %, its maximum flame height was 177.92 mm, the lowest of all conditions, and there was a maximum value of 237.44 mm when the percentage is 60 %, which was an increase of 25 %. Before the mixed extinguishing media was introduced for 40 s, the flame heights when the percentage of *trans*-1233zd was 20 % were lower than the other working conditions. Trans-1233zd may contribute to some extent to the role of Novec 1230 in intensifying combustion. To quantify the synergistic effect of the two substances, the theoretical MEC without considering the synergistic effect was calculated according to **Eq. (3)**, whose comparison with the experimental values is shown in

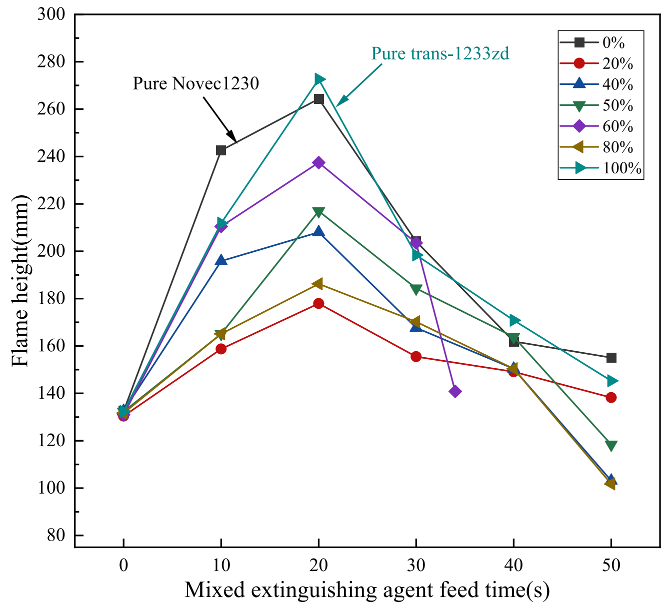


Fig. 4. Effect of different ratios of *trans*-1233zd on flame height.

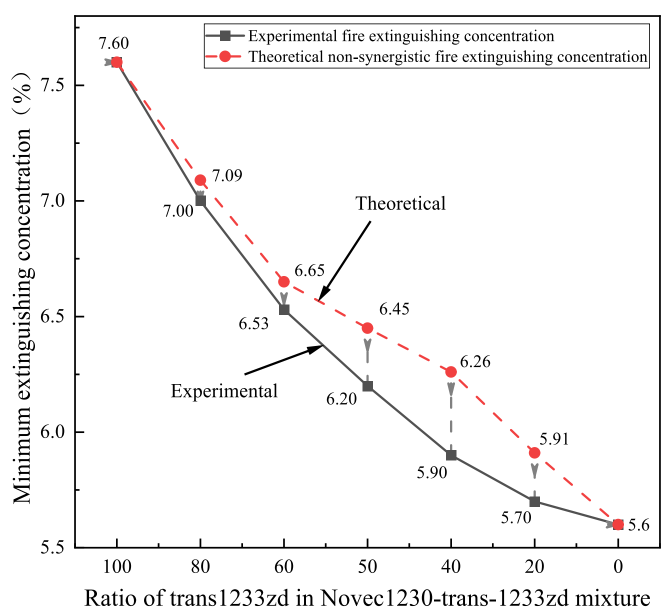


Fig. 5. The experimental and theoretical MEC of Novec-1230 and *trans*-1233zd.

Fig. 5. As the volume fraction of *trans*-1233zd in the mixed extinguishing media decreases, the experimental MEC also decreases gradually. When the volume fraction of tran-1233zd varied from 80 % to 20 %, the theoretically calculated values of MECs were 7.09 %, 6.65 %, 6.45 %, 6.26 % and 5.91 %, which converged to a straight line. In comparison, the experimentally measured MECs were 7.00 %, 6.53 %, 6.20 %, 5.9 % and 5.7 % respectively, which is shown as a curved line. When *trans*-1233zd is 40 %, there was the maximum difference between the two, compared with the theoretical value of 6.26 %, the experimental value was 5.9 %, at a decrease of 5.75 %. The experimental value is always lower than the theoretical, indicating that Novec1230 and *trans*-1233zd have a positive synergistic effect in the flame suppression process. To further check the synergistic effect of Novec1230 and *trans*-1233zd, the synergistic factor in flame suppression of mixed extinguishing media in different ratios was calculated according to **Eq** (2), and the results were shown in Fig. 5. The synergy factor F gradually increases as the percentage of *trans*-1233zd in the mixed fire extinguishing media increases. Among all the ratios, the synergy factor had the minimum value of 0.94 when *trans*-1233zd is 20 %, implying the best synergy at that condition. The synergistic factor $F < 1$, proves the conclusion that there is a positive synergistic effect between the two gases (see Fig. 6.).

3.3. The potential mechanism of synergistic effect

3.3.1. The main pyrolysis products of Novec1230 during fire

Many researchers have studied the pyrolysis process and products of Novec 1230 [9,44]. It has been found that Novec 1230 starts to pyrolyze violently when the temperature interval ranges from 650 to 700 ℃. In nitrogen atmosphere, the gaseous pyrolysis products include CO, $CF_2{=}CF_2$, C_3F_8, $CF_3CF{=}CF_2$, C_4F_{10}, $CF_3CF_2CF{=}CF_2$, $CF_3CF{=}CFCF_3$, $CF_2{=}CCF_3CF_3$, and C_5F_{12}. When the temperature is lower than 700 ℃, C_5F_{12} is the main product [44]. With the temperature continuing to increase, the C_5F_{12} begins to pyrolyze, C_4F_{10} and $CF_3CF{=}CF_2$ begin to gradually increase. When the temperature approaches 750 ℃, C_4F_{10} and $CF_3CF{=}CF_2$ are found to be the two main pyrolysis products [44]. During the fire extinguishing experiment, thermocouples were placed at the flame. In the fire extinguishing process, the highest temperature could reach 1000 ℃. It can be considered that Novec 1230 has the conditions for pyrolysis in this environment. Therefore, the main pyrolysis products of Novec1230 are C_5F_{12}, C_4F_{10} and $CF_3CF{=}CF_2$. The above major pyrolysis products are mapped and structurally optimized by using Gaussian 16 code, as shown in Fig. 7.

3.3.2. The main pyrolysis products of trans-1233zd

According to previous studies [45], *trans*-1233zd starts to pyrolyze when the temperature approaches 400 ℃. As the temperature increased, the pyrolysis of *trans*-1233zd intensified. In argon atmosphere, when the temperature approaches 450 ℃, $CH{\equiv}CCF_3$, $C_4H_2F_6$, $CH{\equiv}CCl$, $CH_2{=}CHCl$ and C_4HF_6Cl begin to appear in the pyrolysis products. When the temperature approaches 700 ℃, *trans*-1233zd was almost completely decomposed. By analyzing the pyrolysis products of *trans*-1233zd, the percentage contents of $CF_2{=}CHCHFCl$, CF_3CH_2CCl and CF_3CH-$CHCl$ are high. During fire extinguishing experiment, the highest temperature reached 1000 ℃, so these three can be seen as the main pyrolysis products of *trans*-1233zd. The above major pyrolysis products are mapped and structurally optimized by using Gaussian 16 code as shown in Fig. 8.

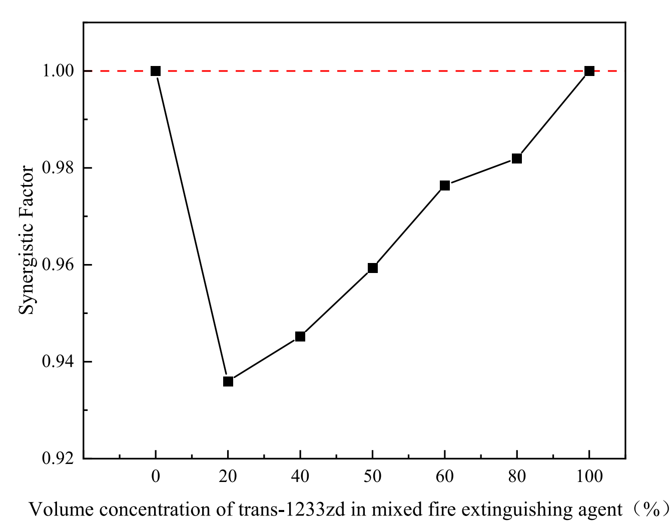
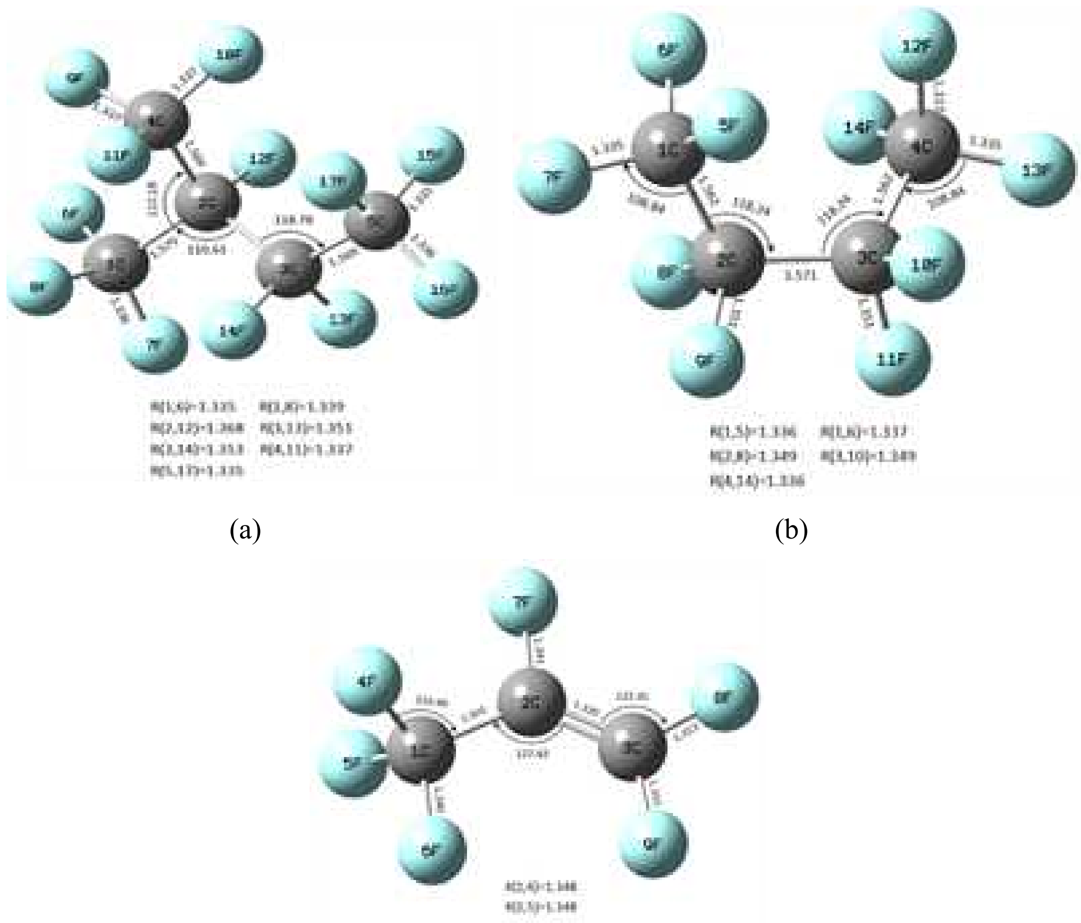


Fig. 6. Changes in synergy factor at different *trans*-1233zd volume concentrations in mixed fire extinguishing media.



(a) (b) (c)

Fig. 7. The main pyrolysis products of Novec1230. (a) C_5F_{12} (b) C_4F_{10} (c) $CF_3CF{=}CF_2$.

3.3.3. *The synergistic reaction process*

To reveal the synergistic mechanism of mixed fire extinguishing media, it is necessary to investigate the reactions that exist between the pyrolysis products of Novec 1230 and *trans*-1233zd. The major pyrolysis products of Novec1230 and *trans*-1233zd are C_5F_{12}, C_4F_{10}, $CF_3CF{=}CF_2$, $CF_2{=}CHCHFCl$, CF_3CH_2CCl and $CF_3CHCHCl$. The reactions between the major products present in Novec 1230 and *trans*-1233zd were simulated using the Gaussian 16 code, and the results are given below.

Reaction paths 1, 2 and 3 are the three reactions of the pyrolysis product of *trans*-1233zd, $CF_2{=}CHCHFCl$, with C_5F_{12}, C_4F_{10} and C_3F_6. The respective energy barriers and transition states TS1, TS2 and TS3 as shown in Fig. 9, Fig. 10 (a), (b) and (c). Path 1 with TS1 generates P1 by overcoming the energy barrier of 692.65 kJ·mol^{-1}, during which the C-F bond on $CF_2{=}CHCHFCl$ is broken to produce •F and $\cdot CF{=}CHCFHCl$, the C–C bond on C_5F_{12} is broken to produce $\cdot CF_2$, $\cdot CF_3$ and $\cdot C_3F_6$. The other $\cdot CF_3$ is created by ·F and $\cdot CF_2$ visa an addition reaction. Path 2 with TS2 generates P2 by overcoming the energy barrier of 439.19 kJ·mol^{-1}. The decomposition of C_4F_{10} produces $\cdot C_2F_5$, $\cdot CF_3$ and $\cdot CF_2$, and $\cdot CF_2$ produces another $\cdot CF_3$ through an addition reaction with ·F, which is the source of the two $\cdot CF_3$ in P2. $CF_2{=}CHCHFCl$ and C_3F_6 generate P3 with TS3 by overcoming the energy barrier of 722.74 kJ·mol^{-1}. The $\cdot C_3F_7$ in P3 is produced by the addition of ·F and C_3F_6.

Reaction paths 4,5 and 6 are the three reactions of the pyrolysis product of *trans*-1233zd, CF_3CH_2CCl, with C_5F_{12}, C_4F_{10} and C_3F_6. The energy barriers, reaction products P4, P5 and P6, and transition states TS4, TS5 and TS6 are shown in Fig. 9, Fig. 10 (d), (e) and (f). CF_3CH_2CCl and C_5F_{12} with TS4 generate P4 by overcoming the energy barrier of 529.67 kJ·mol^{-1}. In this process, the C-F bond in CF_3CH_2CCl is broken to produce ·F and $\cdot CF_2CH_2CCl$, and the C–C bond in C_5F_{12} is broken to produce $\cdot CF_2$, $\cdot CF_3$, and $\cdot C_3F_7$. CF_4 is created by the addition of ·F and $\cdot CF_3$. CF_3CH_2CCl and C_4F_{10} with TS5 generate P5 by overcoming the energy barrier of 545.87 kJ·mol^{-1}, where C_4F_{10} decomposes to produce $\cdot C_2F_5$, $\cdot CF_2$ and $\cdot CF_3$. CF_4 is obtained by the addition of ·F and $\cdot CF_3$. The product P6 was obtained from CF_3CH_2CCl and C_3F_6 with TS6 by overcoming an energy barrier of 627.14 kJ·mol^{-1} and consisted of $\cdot CF_2CH_2CCl$ and $\cdot C_3F_7$, where $\cdot C_3F_7$ was obtained by addition of C_3F_6 and ·F.

Reaction paths 7, 8 and 9 are the three reactions of $CF_3CHCHCl$ and C_5F_{12}, C_4F_{10} and C_3F_6. The products P7, P8 and P9 and the transition states TS7, TS8 and TS9 are shown in Fig. 9 and Fig. 10 (g), (h) and (i). CF_3CH-$CHCl$ and C_5F_{12} with TS7 generate P7 by overcoming the energy barrier of 273.29 kJ·mol^{-1}. P7 consists of $\cdot C_3F_7$, $CF_2CHCHCl$ and 2 $\cdot CF_3$. During the reaction C_5F_{12} decomposes to produce $\cdot CF_3$, $\cdot CF_2$ and $\cdot C_3F_7$. The other $\cdot CF_3$ is created by the addition of $\cdot CF_2$ and ·F which comes from C-F bond breakage in CF_3CH-$CHCl$. The product P8 is produced from CF_3CH-$CHCl$ and C_4F_{10} by overcoming the energy barrier of 273.41 kJ·mol^{-1} with TS8 and consists of $\cdot C_2F_5$,$\cdot CF_2CHCHCl$ and 2 $\cdot CF_3$. One of the $\cdot CF_3$ is produced by the decomposition of C_4F_{10} while the other is obtained by the addition of ·F and $\cdot CF_2$ which comes from the decomposition of C_4F_{10}. The product P9 is obtained from $CF_3CHCHCl$ and C_3F_6 with TS9 by overcoming the energy barrier of 380.14 kJ·mol^{-1} and consists of $\cdot CF_3CF$, $\cdot CF_2CHCHCl$ and $\cdot CF_3$. The decomposition of C_3F_6 during the reaction produces $\cdot CCF_3$ and $\cdot CF_3$, and $\cdot CCF_3$ and ·F produce $\cdot CFCF_3$ via an addition reaction.

The height of the energy barrier shows the magnitude of the energy barrier that needs to be overcome to transform the reactants into

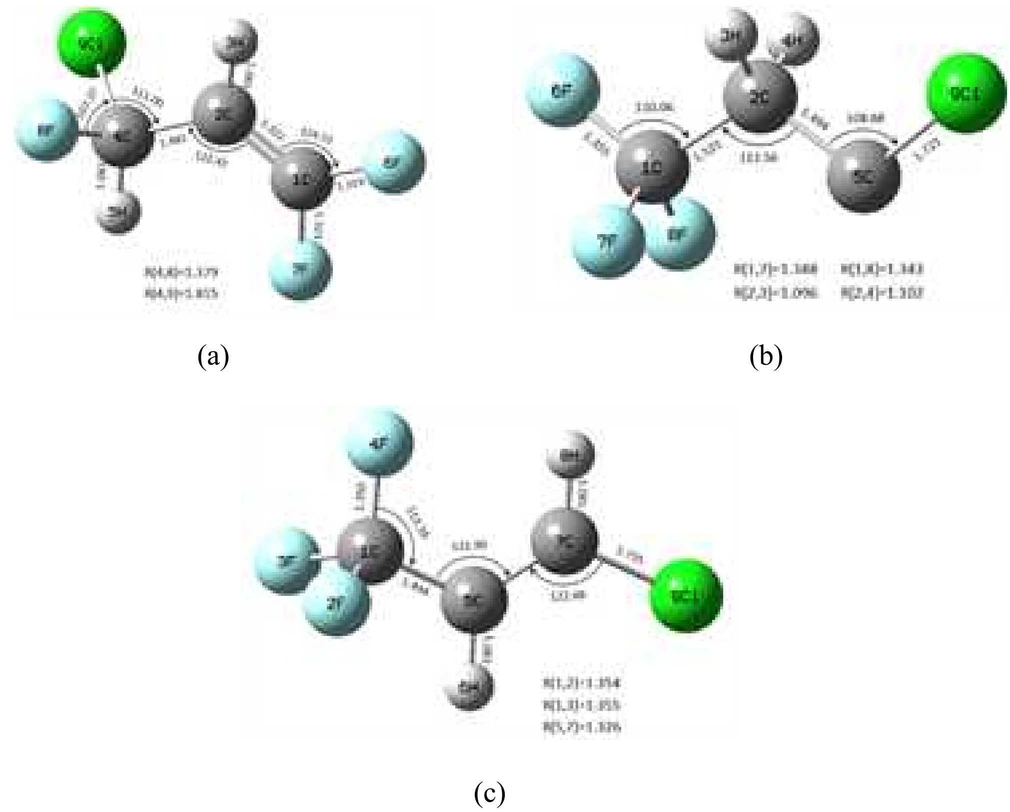


Fig. 8. The main pyrolysis products of *trans*-1233zd. (a) CF_2=CHCHFCl (b) CF_3CH_2CCl (c) $CF_3CHCHCl$.

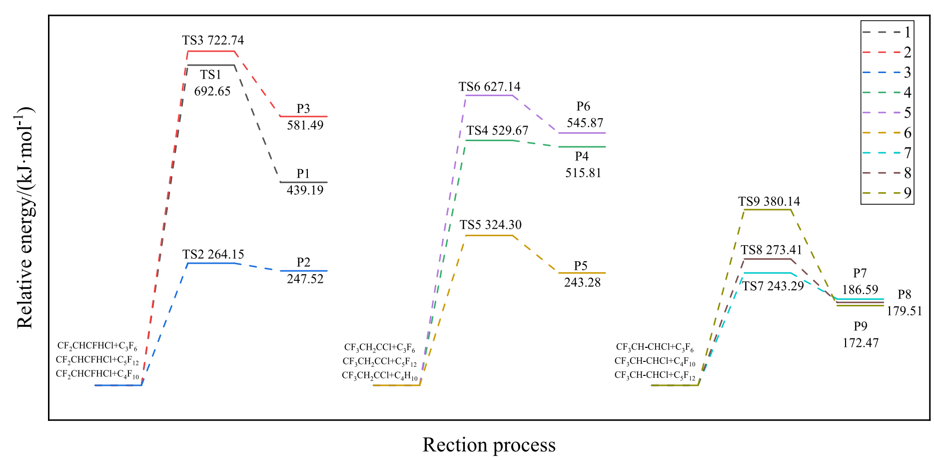


Fig. 9. Energy barriers of reactions.

products. The higher the energy barrier, the more difficult the reaction is. Among the above nine reactions, the lowest energy barriers are P2, P7 and P8 with energy barriers of 247.52 kJ·mol^{-1}, 243.29 kJ·mol^{-1} and 273.41 kJ·mol^{-1}. Therefore, in the fire extinguishing process, the first three reactions occurring are CF_2=CHCHFCl with C_4F_{10}, $CF_3CHCHCl$ with C_5F_{12}, and $CF_3CHCHCl$ with C_4F_{10}. In this process ·C_2F_5, ·$CF_2CHCHCl$, ·CF=CHCFHCl, ·CF_3 and ·C_3F_7 are generated. ·CF_3, ·C_2F_5 and ·C_3F_7 are common groups in hydrofluorocarbon fire extinguishing agents during the flame suppression process, which can react with H and OH in the fire scene [46,47]. Compared with the two existing fire extinguishing agents, the reaction between the pyrolysis products generates more of the three groups. This enhances the elimination reaction of free radicals in the flame and further improves the flame suppression effect. The above conclusions are drawn based on the results of quantum chemical calculations. The reactions between the pyrolysis products need to be further verified through experiments. Compared with Novec 1230, *trans*-1233zd is more easily degraded in the atmosphere, and the degradation products have a shorter residence time in the atmosphere [48]. Therefore, the use of mixed chemical gases helps to reduce the use of Novec 1230 and is more environmentally friendly. The reaction and fire extinguishing synergistic mechanism between the pyrolysis products of Novec1230 and trans1233zd are shown in Fig. 11 and Fig. 12.

4. Conclusions

In this paper, the MEC of Novec 1230 and trans1233zd mixed chemical gases at different volume fractions was tested. The synergy theoretical extinguishing concentration and synergy factor F were

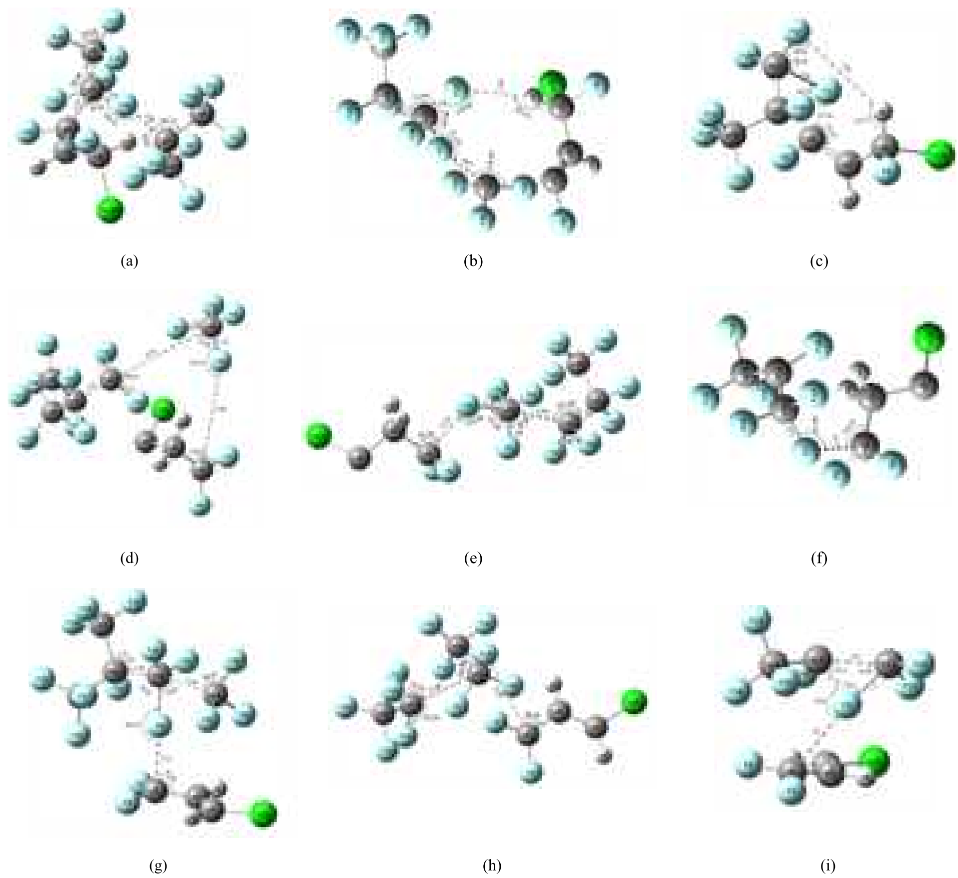


Fig. 10. Structural diagram of the transition state. (a) TS1 (b) TS2 (c) TS3 (d) TS4 (e) TS5 (f) TS6 (g) TS7 (h) TS8 (i) TS9.

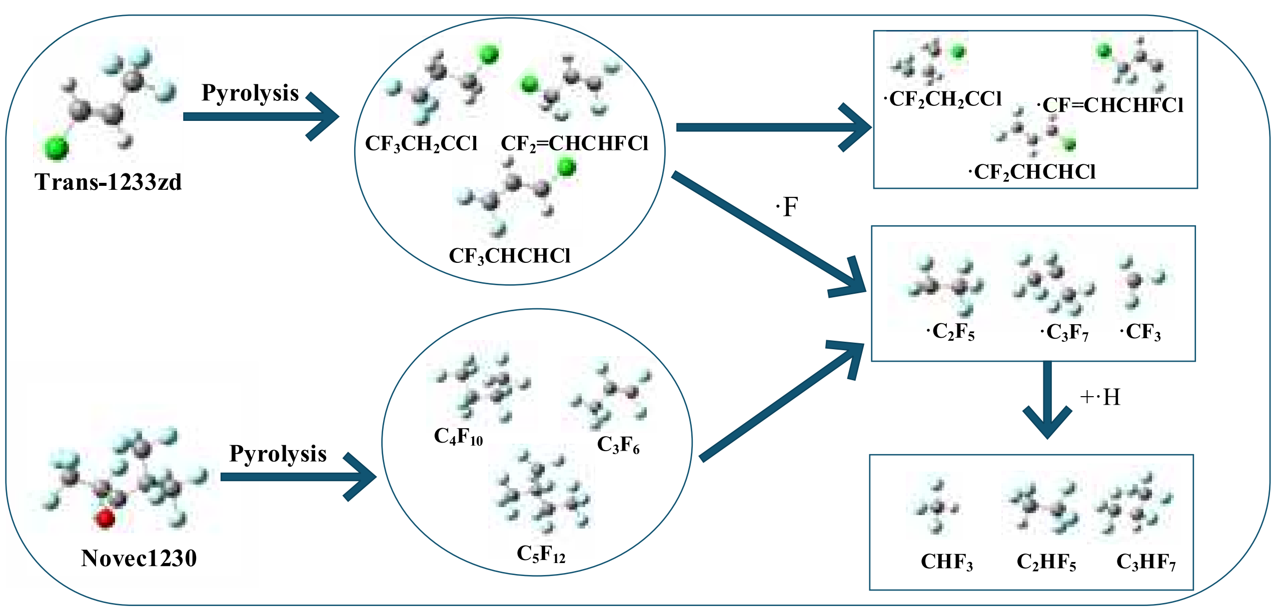


Fig. 11. Reactions between pyrolysis products of Novec1230 and *trans*-1233zd.

calculated and compared with the experimental values. The synergy reaction of the pyrolysis products was obtained by using Gaussian16 code to propose the potential synergistic mechanism between Novec1230 and *trans*-1233zd in the flame suppression process. The results are as follows:

(1) As the volume fraction of *trans*-1233zd reduced, the MEC of the mixed extinguishing medium decrease gradually. When the volume fraction of *trans*-1233zd is 80 %, 60 %, 50 %, 40 % and 20 %, the MEC of the mixed chemical gas is 7.0 %, 6.5 %, 6.2 %, 5.9 % and 5.7 %. When the volume fraction of *trans*-1233zd was 20 %, the flame height was lowest.

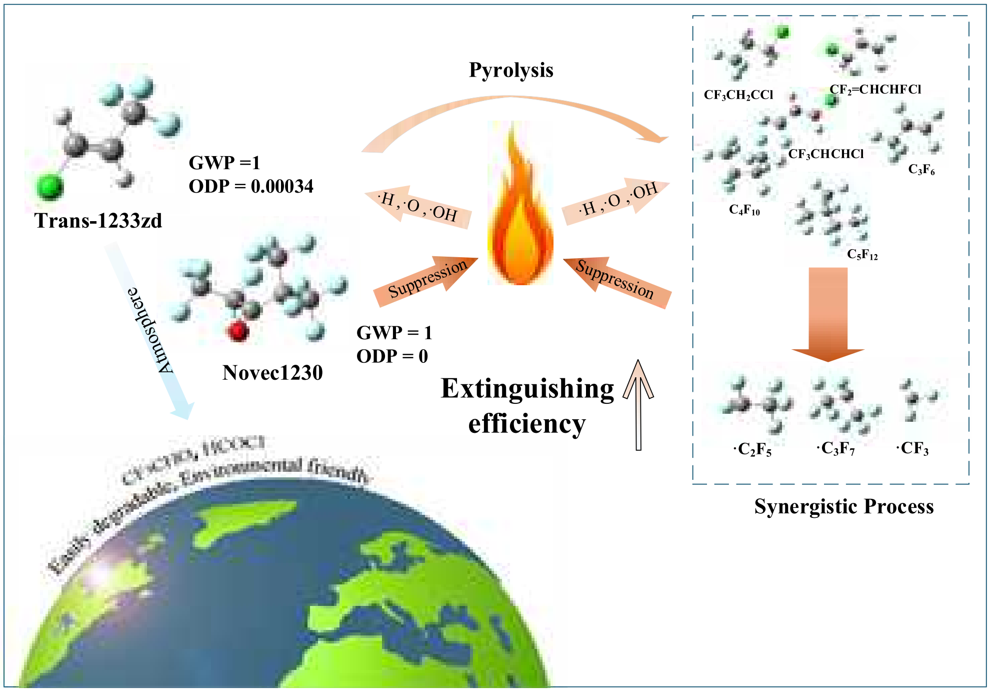


Fig. 12. Synergistic mechanism of mixed extinguishing media in flame suppression process.

(2) The experimental values of the MEC were lower than the theoretical values assuming no synergistic effect, and the synergistic factor F was always less than 1, which indicated the positive synergistic effect of Novec1230 and *trans*-1233zd in flame suppression. When the volume fraction of *trans*-1233zd was 20 %, the synergistic effect was best.

(3) The reactions of pyrolysis products of Novec1230 and trans1233zd is clarified, resulting into the producing of $\cdot C_2F_5$, $\cdot CF_3$ and $\cdot C_3F_7$. The newly generated radicals additionally enhance the fire extinguishing efficiency.

The above results demonstrate the existence of positive synergistic effects of Novec 1230 and *trans*-1233zd in the flame suppression process. Both theoretical and experimental results show that the Novec 1230 and *trans*-1233zd mixed fire extinguishing medium has the potential to become a new generation of chemical gas fire extinguishing agents, which can improve fire extinguishing efficiency and be more environmentally friendly than single agents. However, further testing is needed to study their effectiveness and practical application in depth.

CRediT authorship contribution statement

Biao Zhou: Conceptualization. **Xuyao Wang:** Writing – original draft, Investigation. **Hideki Yoshioka:** Software, Supervision. **Kai Wang:** Project administration, Software. **Dezheng Wang:** Data curation, Formal analysis. **Xin Huang:** Validation, Methodology. **Tao Chen:** Validation. **Yi Li:** Methodology, Software.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work is supported by Beijing Municipal Science and Technology Project (Z231100003823022), the Ordos key research and development program (No.YF20240026), Tianjin Natural Science Foundation Project (22JCZDJC00880), Beijing Nova Program (No. 202504841008), the Key Laboratory of Fire Protection Technology for Industry and Public Building, Ministry of Emergency Management (No.2023KLIB02), the Fundamental Research Funds for the Central Universities (No. 2025ZKPYAQ03), State Key Laboratory Cultivation Base for Gas Geology and Gas Control (Henan Polytechnic University) (No. WS2021A01).

Data availability

Data will be made available on request.

References

[1] L. Zhang, K. Jin, J. Sun, Q. Wang, A review of fire-extinguishing agents and fire suppression strategies for lithium-ion batteries fire, Fire Technol. 60 (2024) 817–858.
[2] A. Ubowska, M. Szczepanek, Engine rooms fire safety–fire-extinguishing system requirements, Zeszyty Naukowe Akademii Morskiej w Szczecinie (2016) 51–57.
[3] W. Ke, W. Yang, B. Zhou, K. Wang, J. Sun, X. Sun, M. Xu, Q. Chen, B. Qiu, W. Wang, The color change analysis of historic wooden remains after fire-suppression by fluorinated chemical gases, Heritage Science 9 (2021) 93.
[4] W.K. Chow, E. Lee, F. Chau, J. Dyke, The necessity of studying chemical reactions of the clean agent heptafluoropropane in fire extinguishment, Archit. Sci. Rev. 47 (2004) 223–227.
[5] T. Wang, Y.-J. Hu, P. Zhang, R.-M. Pan, Study on thermal decomposition properties and its decomposition mechanism of pentafluoroethane (HFC-125) fire extinguishing agent, J. Fluor. Chem. 190 (2016) 48–55.
[6] X. Zhou, B. Zhou, Comprehensive theoretical and experimental studies on the CF3H fire-extinguishing mechanism, Chin. J. Chem . 29 (2011) 1335–1350.
[7] H. Xing, S. Lu, H. Yang, H. Zhang, Review on research progress of C6F12O as a fire extinguishing agent, Fire 5 (2022) 50.
[8] W. Xu, Y. Jiang, X. Ren, Combustion promotion and extinction of premixed counterflow methane/air flames by C6F12O fire suppressant, J. Fire Sci. 34 (2016) 289–304.
[9] H. Xing, Y. Cheng, S. Lu, N. Tao, H. Zhang, A reactive molecular dynamics study of the pyrolysis mechanism of C6F12O, Mol. Phys. 119 (2021) e1976425.
[10] M.L. Robin, Suppression of class a fires with HFC-227ea, Process Saf. Prog. 17 (1998) 209–212.
[11] F. Wang, L. Ye, L. Zhang, Y. Bi, H. Cong, W. Gao, M. Bi, A kinetic study of the inhibition mechanism of HFC-227ea on hydrogen combustion, Combust. Flame 260 (2024) 113262.
[12] Q. Zhou, W. Ma, H. Shi, S. Lu, H. Zhang, Enhancement and suppression of counterflow diffusion flame by HFC-125, Process Saf. Environ. Prot. 180 (2023) 23–34.

[13] Z. Jin, X. Zhang, The fire-extinguishing performance and mechanism of fluorinated cyclobutane through experimental measurement and numerical calculation, New J. Chem. 47 (2023) 15787–15796.
[14] Q. Yang, J. Zhang, Y. Gao, X. Zhou, H. Zhang, Toward better Halon substitutes: Effects of H content on pyrolytic and fire-suppressing mechanisms of ozone-friendly fluorinated alkanes, J. Mol. Struct. 1285 (2023) 135506.
[15] 3M, <3m-novec-1230-fire-protection-fluid.pdf>.
[16] Honeywell, Solstice® zd (R-1233zd).
[17] Z. Lv, Z. Yang, Y. Zhang, Y. Chen, J. Li, A comparative investigation on the flame inhibition characteristics and mechanism of 1, 1, 2, 3, 3, 3-hexafluoro-1-propene (R1216), Fuel 324 (2022) 124652.
[18] B. Feng, Z. Zhang, L. Jian, D. Wang, R. Feng, X. Wang, G. Zhao, X. Guo, S. Ma, Effect of two halogenated olefins on combustion characteristics of Isobutane, Fuel 360 (2024) 130545.
[19] X. Wang, H. Tian, G. Shu, Z. Yang, Insight into the flammability limit and combustion reactions behaviors of R1233zd (E)/R1270 mixtures refrigerants, Int. J. Refrig (2025).
[20] Z. Zhao, J. Luo, K. Yang, D. Zou, Q. Wang, G. Chen, Experimental study on the influence of flame retardants on the flammability of R1234yf, J. Loss Prev. Process Ind. 81 (2023) 104945.
[21] J.L. Pagliaro, G.T. Linteris, P.B. Sunderland, P.T. Baker, Combustion inhibition and enhancement of premixed methane–air flames by halon replacements, Combust. Flame 162 (2015) 41–49.
[22] T. Bolshova, V. Shvartsberg, A. Shmakov, Synergism of trimethylphosphate and carbon dioxide in extinguishing premixed flames, Fire Saf. J. 125 (2021) 103406.
[23] X. Cao, J. Zhou, Y. Lu, Z. Wang, Z. Wang, Research on the synergy effect of water mist containing additives and flame-retardant system on the syngas explosion inhibition, Appl. Therm. Eng. 255 (2024) 124004.
[24] L. Wang, Y. Liang, Y. Hu, W. Hu, Synergistic suppression effects of flame retardant, porous minerals and nitrogen on premixed methane/air explosion, J. Loss Prev. Process Ind. 67 (2020) 104263.
[25] B. Pei, Y. Han, L. Chen, Z. Hu, Z. Wu, H. Lv, W. Ji, Study on the synergistic suppression effect and mechanism of N2/ultrafine water mist on liquefied petroleum gas explosion, ACS Omega 9 (2024) 14539–14550.
[26] Z. Tianwei, L. Hao, Z. Han, W. Yong, G. Zidong, W. Chaoqing, Experimental study on the synergistic effect of fire extinguishing by water and potassium salts, J. Therm. Anal. Calorim. 138 (2019) 857–867.
[27] F. Chen, B. Yao, W. Guo, G. Zhu, T. Xu, T. Deng, Z. Jiang, Z. Wang, M. Peng, X. Wang, Experiment study on fire extinguishing effects of airflow-water synergistic jet, Case Stud. Therm. Eng. 49 (2023) 103367.
[28] C. Lu, Z. Su, S. Chen, Q. Meng, C. Ban, Z. Duan, J. Liu, M. Yu, Prevention effect of the synergistic of C6F12O and inert gas on methane explosion, J. Saf. Environ. 23 (2023) 1115–1123.
[29] J. Ma, X. Xian, Q. Zhao, H. Wang, Study on the synergistic fire extinguishing efficiency of C6F12O/N2 mixed N2, Fire Sci. Technol. 43 (2024) 850–854+866.
[30] Y. Li, X. Zhang, S. Tian, S. Xiao, Y. Li, D. Chen, Insight into the decomposition mechanism of C6F12O-CO2 gas mixture, Chem. Eng. J. 360 (2019) 929–940.
[31] T. Yu, Y. Wang, J. Chen, W. Ji, B. Gao, J. Zhu, S. Qin, Applicability of HFC-227ea/CO2 for battery energy storage systems safety: Insights from explosion suppression experiments and kinetic analysis, Int. J. Hydrogen Energy 97 (2025) 1424–1439.
[32] K. Yang, Y. Jia, H. Ji, Z. Xing, J. Jiang, Explosion mitigation of methane–air mixture in combined application of HFC-227ea/CO2 and ultrafine water mist in the pipeline, Process Saf. Prog. 43 (2024) S273–S283.
[33] Z. Tianwei, L. Hao, S. Jiwei, W. Bo, W. Yong, S. Xinchen, G. Zidong, Synergistic inhibition effect on lithium-ion batteries during thermal runaway by N2-twin-fluid liquid mist, Case Stud. Therm. Eng. 37 (2022) 102269.
[34] T. Liang, D. Liu, Y. Wang, Effect of DMMP on the minimum extinguishing concentration of typical fire extinguishing agent, Safety Environ. Eng. 28 (2021) 44–48.
[35] V.R. Katta, F. Takahashi, V. Babushok, Effects of agent blending on fire-suppression characteristics, AIAA scitech 2019, Forum (2019) 2373.
[36] T. Liang, L. Dezhi, W. Yongjin, W. Zhong, Z. Jun, Study on fire extinguishing efficiency of the mixtures of C6F12O and (C2F5) 3N, CIESC Journal 71 (2020) 3387.
[37] T. Chen, D. Lu, C. Hu, L. Jing, X. Fu, X. Zhou, Study on the test of critical fire extinguishing concentration of perfluorohexanone fire extinguishing agent, Fire Sci. Technol. 34 (2015) 1210–1214.
[38] V.L. Deringer, A.P. Bartók, N. Bernstein, D.M. Wilkins, M. Ceriotti, G. Csányi, Gaussian process regression for materials and molecules, Chem. Rev. 121 (2021) 10073–10141.
[39] R.J. Bartlett, Many-body perturbation theory and coupled cluster theory for electron correlation in molecules, Annu. Rev. Phys. Chem. 32 (1981) 359–401.
[40] L. Vereecken, J.S. Francisco, Theoretical studies of atmospheric reaction mechanisms in the troposphere, Chem. Soc. Rev. 41 (2012) 6259–6293.
[41] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, Phys. Rev. 136 (1964) B864.
[42] D.R. Salahub, M.C. Zerner, The challenge of d and f electrons: theory and computation, ACS Publications, 1989.
[43] J.L. Lott, S.D. Christian, C.M. Sliepcevich, E.E. Tucker, Synergism between chemical and physical fire-suppressant agents, Fire Technol. 32 (1996) 260–271.
[44] T. Wang, P. Zhang, R. Pan, Investigation of the High Temperature Pyrolysis Behavior of Perfluorohexanone as an Environmental-Friendly Fire Extinguishing Agent, Pin and Pan, Renming, Investigation of the High Temperature Pyrolysis Behavior of Perfluorohexanone as an Environmental-Friendly Fire Extinguishing Agent, (2024).
[45] R. Wu, X. Wang, L. Cheng, C. Ren, X. Wei, X. Zhang, Experimental and theoretical studies on the thermal decomposition of trans-1-chloro-3, 3, 3-trifluoropropene and 2-chloro-3, 3, 3-trifluoropropene and their fire-extinguishing performance, New J. Chem. 44 (2020) 12932–12941.
[46] H. Fukaya, T. Ono, T. Abe, Ab initio molecular orbital study of reaction of pentafluoroethyl radical with hydroxyl and hyrogen radicals, Bull. Chem. Soc. Jpn 72 (1999) 207–211.
[47] R. Hynes, J. Mackie, A. Masri, Inhibition of premixed hydrogen-air flames by 2-H heptafluoropropane, Combust. Flame 113 (1998) 554–565.
[48] M. Sulbaek Andersen, O. Nielsen, M. Hurley, T. Wallington, Atmospheric chemistry of t-CF3CH= CHCl: products and mechanisms of the gas-phase reactions with chlorine atoms and hydroxyl radicals, PCCP. Phys. Chem. Chem. Phys. (Print) 14 (2012) 1735–1748.